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Current Opinion in Chemical Engineering

Magnetic resonance in reaction engineering: beyond spectroscopy

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Magnetic resonance (MR), in the form of nuclear magnetic resonance (NMR) spectroscopy, is well established in characterising catalysts and studying relatively small catalytic samples *in situ*. However, MR-based measurements of molecular adsorption and diffusion, along with MR micro-imaging and flow mapping offer an additional toolkit of methods to study both the catalyst and its working environment. Focussing on recent advances in the implementation of MR methods in reaction engineering we consider MR measurements yielding information at two quite different length-scales: first, the ability of MR relaxometry and diffusometry to study molecular adsorption and diffusion processes within the pore space of heterogeneous catalysts; second, the use of micro-imaging and MR flow imaging to critically evaluate the closure relationships and boundary conditions used in numerical simulations of catalytic reactor operation.

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Introduction

When considering the role of magnetic resonance (MR) in catalysis, we naturally think of nuclear magnetic resonance (NMR) spectroscopy as used for the characterisation of solid state structure and speciation of the catalyst surface [1–6,7•]. Alongside these advances, an increasing diversity of MR techniques for studying catalytic function *in situ* has been pioneered by a number of groups. *In situ* NMR methods can be broadly divided into two main areas: those methods that operate under 'batch' conditions in sealed vessels [8–10] and those that operate under 'flow' conditions [11,12,13••]. The motivation for the vast majority of these studies has been to access chemical information — for example, the characterisation of acidic and basic sites at the catalyst surface, the oxidation state of surface active species, identification of particular mechanistic steps in the catalytic conversion. In modelling a catalytic process, clearly the chemical engineer not only needs this information but also gives consideration to the interplay between the chemical processes occurring and the influence of the associated rates of adsorption, desorption and mass transfer within the catalyst, as well as the local boundary conditions imposed on the catalyst by the hydrodynamic characteristics of the given reactor environment.

Despite the limitations of MR in not being able to study samples and sample environments containing significant amounts of ferromagnetic material, MR remains one of the few measurement methods which can provide chemical information via spectroscopic measurement, while in the same sample environment being able to measure molecular transport without need for use of tracers or invasive probes; all these measurements can be made in optically opaque media [14,15•]. This article attempts to illustrate how MR methods, which complement spectroscopic data, are now sufficiently advanced and robust that they can begin to yield valuable information at the microscale where we can probe molecular adsorption and diffusion phenomena, while at the macroscale we can critically evaluate the assumptions used in theoretical analysis and numerical simulation of reactor behaviour. The toolkit of MR techniques now available to the chemical engineer can help us understand the relative importance of different chemical and physical phenomena in determining catalytic performance and hence gain insight into improving catalyst and reactor design, and process operation.

The microscale: what is happening inside the pore?

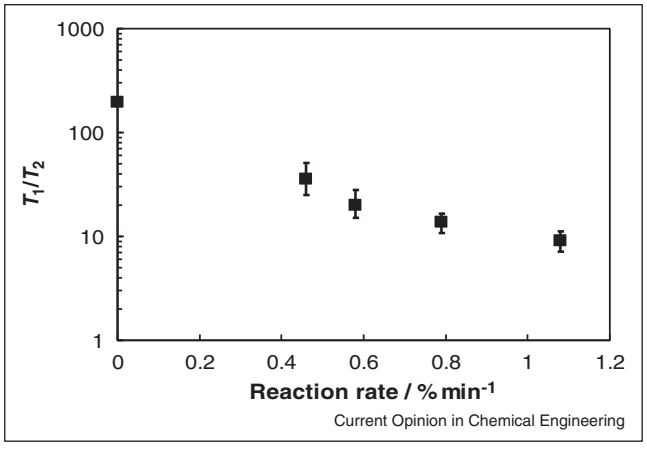
What information might we require to aid our ability to design a catalyst, and to understand and predict catalyst behaviour? Of particular interest are the following questions:

- Which species dominate at the pore surface?
- How does molecular mobility vary within the pore? Is there a strong influence from the surface which restricts

molecular transport close to the surface? If so, can we quantify it?
- Can we decouple the influences of adsorption and diffusion inside the pore?
- Can we predict the way multi-component mixtures behave inside a catalyst pore?

Not only should answers to these questions advance our ability to design and select catalysts with preferred activity and selectivity characteristics, but also the measurements obtained will provide input data and validation of input data to kinetic schemes used in understanding catalyst function and aiding catalyst design. In this regard, it is useful to think of these measurements as another tool to add to those already used in implementing microkinetic analyses. Using a microkinetic approach only the kinetically significant steps are included in the kinetic scheme and then using theoretical principles, numerical simulation (e.g. application of Density Functional Theory) or experimental measurement, the kinetics of each of these steps are quantified — thereby producing a quantitative description of the overall process [16••]. Excellent examples of the approach in use have been reported [17–19]. One of the powerful attributes of MR is that the individual methods are readily implemented under reaction conditions. Indeed, it will be useful to use MR techniques to characterise adsorption and diffusion processes as a function of temperature and pressure to explore how accurately we can predict multi-component transport processes and phase behaviour under realistic operating conditions.

Figure 1



Plot of T_1/T_2 values characterising the strength of surface interaction between five different solvents and a Pt/TiO_2 catalyst. The T_1/T_2 ratio for the reactant phenylbutan-2-one is 49. It is clearly seen that as the strength of the solvent interaction with the surface increases, the rate of conversion decreases. In order of decreasing T_1/T_2 ratio the solvents used are tetrahydrofuran (197), 1,2-dichloroethane (36), 4-tert-butyltoluene (20), cyclohexane (14) and *n*-hexane (9).

Which species dominate at the pore surface? The recent implementation of this measurement came from parallel work undertaken in characterising rock-core wettability, as required for developing oil recovery processes [20]. In this field two-dimensional MR relaxometry experiments are used to characterise the relative strength of interaction of hydrocarbon and aqueous species with the interior surface of the rock — the parallel between hydrocarbon/brine/rock and a multi-component mixture within a solid catalyst is obvious. These experiments are based on simple, robust measurements of nuclear spin relaxation times; relaxation times characterise the return of the nuclear spin system to equilibrium following excitation of the nucleus of interest using radio-frequency excitation. In particular, the spin–lattice (T_1) and spin–spin (T_2) relaxation times are measured. The higher the value of the T_1/T_2 ratio of a given chemical species, the greater the strength of interaction between that species and the surface. Motivated by a study of 2-butanone hydrogenation in mixed 2-propanol/water solvents, this methodology was used to demonstrate the relative strengths of interaction of water, an alcohol (2-propanol) and a ketone (2-butanone) with Pd/Al_2O_3 and Ru/Al_2O_3 catalysts [21].

A very recent example of using this method to guide solvent selection for the hydrogenation of phenylbutan-2-one is shown in Figure 1, which shows the T_1/T_2 data and reaction rate data acquired for phenylbutan-2-one in the presence of five different solvents. In this example, we see that the relative strength of interaction between the individual species is significantly different. A clear correlation between reaction rate and the relative strength of surface interaction of the reactant species compared to the solvent species was observed; the less competitive the solvent is for the catalyst surface, the faster the reaction rate. No correlation was observed between polarity and hydrogen solubility characteristics of the solvents. Although these experiments are, in principle, straightforward, care must be taken in performing the two-dimensional inversion of the data from which the final T_1–T_2 spectrum is obtained [22]; and there remains further research to be done to optimise the implementation of this approach to study complex multi-component inside catalyst pores. The method becomes increasingly challenging if ^{13}C observation is employed due to the far lower MR sensitivity and natural abundance of the ^{13}C nucleus. However, the advantage of using ^{13}C is that due to the far greater spectral range of ^{13}C compared to ^{1}H, it is significantly easier to discriminate between the multiple spectral resonances present in a typical reaction mixture.

There are a number of ways in which these experiments can be used and it becomes important to design experiments that answer the specific question of interest. For example, in the example shown here, the approach has been used to identify a solvent which will maximise

reaction rate — as long as competitive adsorption of the reactant and solvent is the rate-determining step.

How does molecular mobility vary inside a pore? If relaxometry techniques show promise in characterising competitive adsorption processes under *in situ* or *operando* conditions, to what extent can we characterise molecular mobility with a pore? The use of Pulsed Field Gradient (PFG) MR techniques [23••,24] for measuring molecular diffusion is well established and has been demonstrated in application to studying catalytic materials in both its spatially unresolved and resolved modalities [25,26]. By measuring the molecular self-diffusion coefficient in the bulk liquid and inside the pore space a value of the tortuosity of the catalyst pellet is obtained. This is useful measurement but is it the whole story? The measurement is providing an average measure of the molecular diffusion from the entire pore space inside the catalyst. It is generally accepted that a liquid-saturated pore contains two distinct regions with differing molecular dynamics; the majority of the pore is filled with liquid that behaves as if it were similar to a bulk liquid. However, at the pore surface, the molecular dynamics are altered by interactions (adsorption) at the solid surface and limited free diffusion paths. This surface behaviour is considered typically to extend to liquid molecules with one to three monolayers from the pore surface [27,28]. By implementing a more complex version of the basic PFG experiment known as the alternating pulsed gradient stimulated echo (APGSTE) sequence [29], it has been possible to acquire data at more extreme signal attenuations and in the presence of the large 'background' magnetic field gradients that characterise inorganic porous media, thereby enabling measurement of the much slower diffusion processes in the 'surface-influenced' layer as well as the diffusion occurring in the 'bulk' of the pore space [30]. Considering the case of diffusion of 1-octene in a 1 wt% Pd/Al_2O_3 catalyst, this approach has been used to determine two molecular diffusion coefficients of 1.3×10^{-9} and 1.7×10^{-11} $m^2 s^{-1}$ for 'bulk' pore and surface diffusion, respectively. Confirmation that this lower diffusion coefficient is indeed associated with a surface interaction, as opposed to a secondary population of smaller pores, was obtained by treating the catalyst with a silane surface coating, which removed the interaction between the 1-octene and the hydroxyls originally present on the alumina surface; under these conditions the slower diffusion coefficient was no longer observed.

How should we use this type of measurement? The direct measurement of molecular diffusivity will have immediate value as input to models of catalytic reactor processes. These measurements also inform us as to how changes to the catalyst formulation or surface treatment might influence catalyst performance. It is also interesting to examine how such a measurement relates to the predictions of numerical simulations of the same process. This has been done in a comparison of PFG MR determinations of bulk pore and surface diffusion of isopropanol in γ-alumina, with values predicted by molecular dynamics simulation [31]. Excellent agreement was observed between the MR values and the numerically predicted values; the simulated values suggested that the surface-influenced layer as probed by MR comprised the first two molecular layers interacting with the surface.

Can we separate the influences of adsorption and diffusion on catalyst reactivity and conversion? How are molecule-molecule interactions and dynamics influenced by confinement within the pores of catalytic materials? A natural extension of the ideas described previously is to use MR relaxometry and diffusometry to investigate if we can discriminate between the relative importance of the strength of the adsorption interaction and the molecular mobility within the pore in determining catalyst performance; of course, these will be strongly correlated close to the catalyst surface. Recently, the two approaches have been used to probe the effect of water on the catalytic oxidation of 1,4-butanediol in methanol over a Au/TiO_2 catalyst [32]. The presence of water causes a significant reduction in conversion. Using MR this reduction in conversion was shown to be accompanied by both reduced reactant-surface interaction and reactant diffusivity. More detailed studies suggest that it is possible to identify the adsorption interaction as the greater influence on catalytic performance. Relaxometry and diffusometry also allow us to probe the influence of pore confinement on molecular mobility and the creation or breakdown of molecular networks; these ideas are explored in a recent work by D'Agostino *et al.* [33]. In particular, this work studied the relaxation and diffusion characteristics of a range of organic molecules including alkanes, alcohols and carbonyls contained within porous materials — TiO_2, γ-Al_2O_3 and SiO_2. Both MR probes were sensitive to changes in molecule–molecule interactions and molecular dynamics introduced by confinement within the pore space. Most notably, strong evidence was obtained that polyols demonstrate enhanced mobility when inside the pore space relative to their behaviour in the bulk liquid state; this was interpreted as pore confinement disrupting the extensive intermolecular hydrogen bonding network characteristic of these molecules.

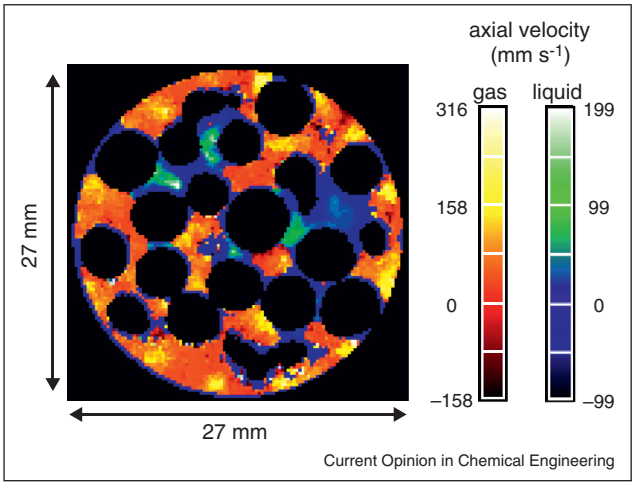
While MR is not the only technique that can probe surface interactions and molecular mobility — vibrational spectroscopy and neutron scattering are obvious examples — it does have a number of attributes which make it a particularly useful method; the ability to identify processes occurring at the pore surface as distinct from measurements averaged within the pore is particularly interesting. It is also worth remembering that MR measurements are readily implemented directly on sample environments operating at any temperature and pressure.

The macroscale: validation of closure laws

The application of MR to imaging hydrodynamics [34,35•,36,37,38•] and mapping chemical conversion [39–41] in reactor environments is well documented. Much of this work has focused on fixed beds. It is now possible to measure directly the average concentration gradients between the intra-pellet and inter-pellet space at different points along the direction of superficial flow along the bed. Can we push these limits of spatial resolution further so that we can determine the concentration gradients at the external surface of individual pellets and see how these relate to the local hydrodynamic boundary conditions on the catalyst pellet and the microstructure of the pellet? Such data would give us a first opportunity to test assumptions used in reactor design. When small % improvements in rate and selectivity become important in reactor operation, the ability to select the catalyst and its operating environment on the basis of direct measurement made during operation under realistic conditions becomes an attractive possibility. A fixed-bed reactor designed to operate under continuous flow conditions at maximum operating conditions of 350°C and 30 bar, and constructed of non-ferromagnetic material, has recently been commissioned in our laboratory. Obviously this reactor offers us the exciting opportunity of performing MR imaging and velocimetry experiments at relatively high temperature and pressure, and can be used to study some catalysts at conditions very close to those they would experience in a working reactor. Just as importantly, the reactor gives us the opportunity to explore how adsorption and diffusion processes vary as a function of temperature and pressure — thereby identifying when it is acceptable to use low temperature/pressure measurements of these characteristics, and to evaluate the accuracy with which these properties can be predicted at relevant operating conditions. The next generation of ultra-fast MR techniques can be expected to offer new opportunities in imaging unsteady flows and chemical conversion with subsecond time resolution. Already, forced pulsing, or periodic operation, of a trickle-bed reactor has been reported and integrated with modelling studies to explore how unsteady state operation of a fixed bed can influence catalyst selectivity and activity — in this example, the hydrogenation of α-methylstyrene was considered [42•]. As well as ^{1}H and ^{13}C spatially resolved spectroscopy to map chemical composition within reactors, the use of parahydrogen to probe the mechanism of catalytic hydrogenations is also being explored [43,44]; opportunities for exploiting parahydrogen and other hyperpolarisation signal enhancement methods [45,46] will almost certainly find niche applications in catalysis.

How else might MR contribute at the macroscale? Imaging multi-phase flows is an area which has seen significant advances over the past five years. With these advances come the opportunities to critically evaluate closure relationships and boundary conditions which are applied in numerical simulations of multi-phase flows and, following incorporation of the appropriate kinetic scheme, full reactor behaviour. This is an area in which the design of the experiment must be given very careful consideration. Examples of this use of MR are now being reported in application to trickle beds, gas–liquid bubble columns and gas–solid fluidised beds; the applications to gas–solid fluidised beds are perhaps the most advanced.

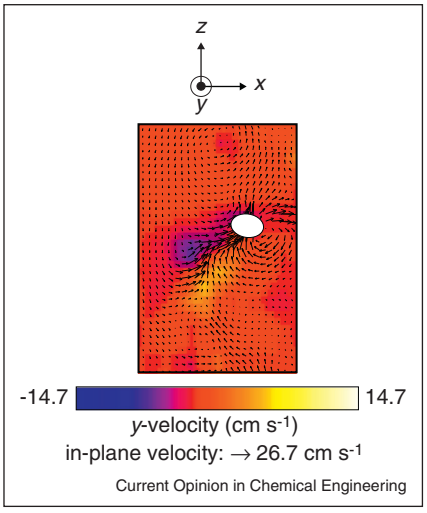
Figure 2



Gas and liquid velocity map of SF_6 (red/yellow) and water (blue/green) during trickle flow. The gas and liquid superficial velocities were 15 mm s^{-1} and 2.3 mm s^{-1}, respectively. Data were recorded for a gas–liquid flow in a 4 cm diameter column packed with 5 mm diameter spheres. The velocity vector measured is the velocity in the direction of superficial flow (i.e. down the bed). ^{19}F imaging is used to image the gas flow. The in-plane spatial resolution of both the gas and liquid flow fields is 234 μm × 234 μm; this was achieved by using a compressed sensing acquisition and image reconstruction for the gas velocity image.

In the context of fixed beds, Figure 2 illustrates the direction in which this work is developing. The figure shows the gas and liquid flow field through a packing of 5 mm spheres (representing catalyst pellets) contained within a 4 cm diameter column. The motivation for acquiring Figure 2 was indeed to explore the closure relationship between gas and liquid velocity [47], and to investigate if the gas–liquid shear stress is significant compared to the liquid solid-shear stress when modelling fixed beds [48,49]. To investigate these phenomena it is necessary to acquire images of the gas and liquid flow field at the highest possible spatial resolution and to acquire the images of both flow fields at the same spatial resolution, thereby minimising mis-registration effects at the gas–liquid interface. The technical challenge here is to overcome the fact that because the gas density is about three orders of magnitude smaller than the liquid density, so too will be the signal-to-noise ratio in the velocity image of the gas phase. The approach used to acquire data

Figure 3



Velocity maps about a single bubble rising freely through stagnant solution. The bubble is of spherically equivalent radius 1.4 mm and the pipe diameter is 16 mm. The location of the bubble was identified from the signal intensity map, and is highlighted by the filled white ellipse. The acquisition rate was 63 fps. The spatial resolution is 390 μm × 586 μm for a field of view of 20 mm × 30 mm.

at this relatively high spatial resolution in the gas phase image has been to undersample the acquired data so that for a fixed acquisition time it is now possible to achieve far greater signal averaging. The particular approach used has been that of Compressed Sensing — a well-established signal processing methodology [50••] but one which has been little used in MR and not hitherto reported in MR flow imaging [51].

Similar undersampling strategies have been used to undersample data acquisitions in application to studying two-phase gas–liquid bubbly flows (Figure 3). Here, signal is being acquired from the liquid phase and so the reduction in number of data points sampled can be exploited directly in increasing the temporal resolution of the images acquired. For this system, two-dimensional velocity maps of a single velocity component of the liquid flow field around air bubbles rising through stagnant water have been acquired at a rate of 188 frames s^{-1} [52]; two-dimensional maps of the v_x, v_y and v_z vector flow fields are acquired at a rate of 63 frames s^{-1}. This imaging capability has the ability to capture bubble and flow field behaviour in real time during bubble coalescence and break-up — these measurements will provide data on which to test our ability to describe coalescence and break-up events in a way which has hitherto been impossible, particularly in high gas voidage systems.

In the field of granular flows, MR has been used in combination with Discrete Element Modelling simulations to discriminate between closure laws on the gas–solid interaction or drag force, and the particle–particle interaction. In both cases MR velocimetry data are recorded for the solids flow. Of course, this requires the solid particles to have an MR signal associated with them and for this reason the solid particles are usually mustard or poppy seeds (which naturally contain oil — and hence ^{1}H), or liquid-filled porous particles [53–55]. The images have then been used to test the accuracy of proposed closure models [56–58]. Among the many results reported in these papers, the work demonstrates that the simulation predictions employing a given closure can agree to differing extents with experiment depending on whether a two-dimensional or three-dimensional geometry is considered. One of the advantages of MR is that the reactor geometry studied can take any size or shape and therefore it is possible to image flows in a three-dimensional column just as easily as a pseudo-two-dimensional flat-walled cell. Various questions arise from these observations — and their analogues exist in experiments performed on gas–liquid and gas–liquid–solid systems. To what extent do closures and multi-phase flow correlations derived from experimental geometries, greatly simplified compared to the real three-dimensional problem, accurately predict three-dimensional behaviour? MR offers the opportunity to begin to explore some of these important challenges.

Conclusions

The ability of MR techniques to image hydrodynamics and chemical conversion is now well known to reaction engineers. The aim of this article has therefore been to introduce some of the emerging areas of application of MR in the field of catalysis and reaction engineering. Recent developments in physical reactor environments that can be operated in a MR magnet, combined with signal processing techniques only recently applied in MR mean that it is now possible to explore phenomena that were previously inaccessible to study by MR — and, in most cases, by any other technique.

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